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<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) Internationales Aktenzeichen: PCT/EP98/06692</p> <p>(22) Internationales Anmeldedatum: 21. Oktober 1998 (21.10.98)</p> <p>(30) Prioritätsdaten: 197 47 890.5 30. Oktober 1997 (30.10.97) DE</p> <p>(71) Anmelder: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düsseldorf (DE).</p> <p>(72) Erfinder: HÖFER, Rainer; Klever Strasse 31, D-40477 Düsseldorf (DE). FIES, Matthias; Dahlienstrasse 26, D-47800 Krefeld (DE).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Bestimmungsstaaten: CA, JP, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p> </td> </tr> </table>			<p>(21) Internationales Aktenzeichen: PCT/EP98/06692</p> <p>(22) Internationales Anmeldedatum: 21. Oktober 1998 (21.10.98)</p> <p>(30) Prioritätsdaten: 197 47 890.5 30. Oktober 1997 (30.10.97) DE</p> <p>(71) Anmelder: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düsseldorf (DE).</p> <p>(72) Erfinder: HÖFER, Rainer; Klever Strasse 31, D-40477 Düsseldorf (DE). FIES, Matthias; Dahlienstrasse 26, D-47800 Krefeld (DE).</p>	<p>(81) Bestimmungsstaaten: CA, JP, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p>
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<p>(54) Title: USE OF DIMERDIOLALCOXYLATE (METH)ACRYLIC ACID ESTERS AS CONSTITUENTS FOR RADIATION CURED COATINGS</p> <p>(54) Bezeichnung: VERWENDUNG VON (METH)ACRYLSÄUREESTERN VON DIMERDIOLALKOXYLATEN ALS BAUSTEINE FÜR STRAHLENHÄRTBARE BESCHICHTUNGEN</p> <p>(57) Abstract</p> <p>The invention relates to acrylic or methacrylic acids of addition products with 1-80 mol ethylene oxide and/or propylene oxide on dimerdiols with a majority of 36-44 C atoms - especially those with a Draize index of less than 2.0 - which are highly suitable as constituents for radiation cured coatings.</p> <p>(57) Zusammenfassung</p> <p>Acryl- und/oder Methacrylsäureestern von Anlagerungsprodukten von 1 bis 80 Mol Ethylenoxid und/oder Propylenoxid an Dimerdiolen mit überwiegend 36 bis 44 C-Atomen - insbesondere solche mit einem Draize-Index von weniger als 2,0 - eignen sich in ausgezeichneter Weise als Bausteine für strahlenhärtbare Beschichtungen.</p>				

Use of Dimerdiolalcoxylate (Meth)Acrylic Acid Esters as Constituents for Radiation Cured Coatings

Field of the Invention

This invention relates to the use of (meth)acrylates of dimerdiol alkoxyates as structural elements for radiation-curing coatings.

Prior Art

5 Acrylates and methacrylates of 1,6-hexandiol are frequently used as structural elements in the production of radiation-curing coatings. 1,6-hexanediol diacrylate, hereinafter referred to in short as HDDA, is preferably used.

For example **US 5,271,968** describes how polycarbonate surfaces
10 are contacted with coating compositions and the curing process is carried out by exposure to UV light. The coating compositions are preferably based on a polyfunctional acrylate monomer, a photoinitiator and HDDA.

Silane-free radiation-curing acrylate-based compositions are known
from **US 5,075,348**. In one preferred embodiment, a special triacrylate is
15 mixed with HDDA.

WO 92/17337 describes UV-curing compositions containing various aliphatic acrylate-based urethanes, including inter alia a multifunctional acrylate which acts as a reactive thinner, trimethylol propane triacrylate and HDDA being particularly preferred.

20 HDDA is distinguished by a low viscosity and an excellent capacity to dissolve epoxy, polyester and urethane acrylates. During curing, the HDDA-containing formulations undergo minimal shrinkage so that coatings on metal, glass and plastics, such as PVC, show excellent adhesion. The cured coatings are particularly resistant to abrasion and to chemicals. The

absence of yellowing and its high gloss predestine HDDA for use in clear coatings for wood and plastics and for clear lacquers on paper. All these properties also make HDDA appear advantageous for pigmented coatings and printing inks.

5 HDDA has a vapor pressure of 0.014 mbar at 50°C and a flash point of 79°C (DIN 51794), so that particular precautions have to be taken for transportation, storage and processing.

Another disadvantage of HDDA is its relatively high skin irritation potential. A measure of this is, for example the so-called Draize index.
10 According to **"Grundlagen und Rezepturen der Kosmetika"** (author: **Karlheinz Schrader**; publisher: **Hüthig**; 2nd Edition 1989), page 1029, the Draize test is one of the most common tests for quantifying skin irritation. In the Draize test, the material to be tested is applied for 24 hours to intact and surface-scarified skin of albino guinea pigs. Erythema and
15 odema readings are taken after 24 and 72 hours on a scale of 0 to 4 or more. As known to the expert, the skin irritation values of 1,6-hexandiol diacrylate (HDDA) are in the range from about 4.4 to >6.

EP 62 807 A1 describes diacrylates of addition products of 2 to 6 moles ethylene oxide and/or propylene oxide onto 1,6-hexanediol,
20 neopentyl glycol and tripropylene glycol and their use as radiation-curing diluents.

Description of the Invention

The problem addressed by the present invention was to provide
25 substances which would be suitable for use as structural elements in the production of radiation-curing coatings and which, at the same time, would have an acceptably low skin irritation potential.

This problem has been solved by (meth)acrylates of dimerdiol alkoxyates which are understood to be acrylic and/or methacrylic acid
30 esters of addition products of 1 to 80 moles ethylene oxide and/or

propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms.

Accordingly, the present invention relates to the use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimer diols predominantly containing 36 to 44 carbon atoms as structural elements for radiation-curing coatings.

Dimerdiols are well-known, commercially available compounds which are obtained, for example, by reduction of dimer fatty acid esters. The dimer fatty acids on which these dimer fatty acid esters are based are carboxylic acids which are obtainable by oligomerization of unsaturated carboxylic acids, generally fatty acids, such as oleic acid, linoleic acid, erucic acid and the like. The oligomerization is normally carried out at elevated temperature in the presence of a catalyst of, for example, clay. The substances obtained (dimer fatty acids of technical quality) are mixtures in which the dimerization products predominate. However, small percentages of higher oligomers, more particularly the trimer fatty acids, are also present. Dimer fatty acids are commercially available products and are offered in various compositions and qualities. Abundant literature is available on the subject of dimer fatty acids, of which the following articles are examples:

- **Fette & Öle 26 (1994), pages 47-51**
- **Speciality Chemicals 1984 (May Number), pages 17, 18, 22-24**

The dimerdiols on which the dimerdiol alkoxylates to be used in accordance with the invention are based are well known among experts, cf. for example a fairly recent article which discusses inter alia the production, structure and chemistry of dimerdiols:

- **Fat Sci. Technol. 95 (1993) No. 3, pages 91-94**

According to the invention, preferred dimerdiol alkoxylates are those which are derived from dimerdiols with a dimer content of at least 50% and, more particularly, 75% and in which the number of carbon atoms per dimer molecule is predominantly in the range from 36 to 44.

5 The (meth)acrylates of dimerdiol alkoxylates may be produced by any known relevant methods known to the expert. They are preferably produced as follows: in a first step, the required diol is contacted with ethylene oxide and/or propylene oxide and the resulting mixture is reacted at temperatures of 20 to 200°C in the presence of an alkaline catalyst. In
10 this way, addition products of ethylene oxide (EO) and/or propylene oxide (PO) onto the particular dimerdiol used are obtained. Accordingly, the addition products are EO adducts or PO adducts or EO/PO adducts with the particular dimerdiol used. In the case of the EO/PO adducts, the addition of EO and PO may be carried out statistically or in blocks. In a
15 second step, the addition products are converted into acrylates and/or methacrylates.

One embodiment of the present invention is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which contain 2 to 20 moles ethylene oxide per mole dimerdiol. The diacrylates of the adducts of about
20 2 to 20 moles ethylene oxide with the required dimerdiol are particularly preferred.

Another embodiment of the invention is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which contain 2 to 20 moles propylene oxide per mole dimerdiol. The diacrylates of the adducts of
25 about 2 to 20 moles propylene oxide with the required dimerdiol are particularly preferred.

A preferred embodiment is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which have a Draize index of less than 2.0 and, more particularly, less than 1.8.

The present invention is not restricted in any way in regard to the intended application of the radiation-curing coatings produced using the (meth)acrylates of dimerdiol alkoxylates to be used in accordance with the invention.

- 5 Finally, the present invention relates to compositions for the production of radiation-curing coatings containing one or more acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols containing 36 to 44 carbon atoms.

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Examples

- The testing of a number of (meth)acrylates of dimerdiol alkoxylates according to the invention showed that these substances are generally compounds which represent effective reactive diluents for radiation-curing coatings and which, in addition, are distinguished by only a slight irritation
15 potential (Draize values <2).

CLAIMS

1. The use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms as structural elements for radiation-curing coatings.
5
2. The use claimed in claim 1, characterized by the use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide which have a Draize index of less than 2.0.
3. Compositions for the production of radiation-curing coatings
10 containing one or more acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms.